

Functional Polymers

Edited by
David E. Dergbreiter and
Charles R. Martin

Texas A&M University
College Station, Texas

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CONTROL OF PHASE STRUCTURE IN POLYMER BLENDS

D. R. Paul

Department of Chemical Engineering
University of Texas
Austin, TX 78712

INTRODUCTION

Development of new molecules and chemical modifications of existing ones have been the most common ways new challenges for polymeric materials have been approached in the past. These routes have become increasingly complex and expensive over the years, and, thus, alternate ones have become more interesting and attractive. Polymer blending is one such approach that is presently in a state of rapid scientific and commercial development, as attested by recent books, reviews, and symposia¹⁻²⁸. Another related physical approach is polymer-polymer composites in the form of fibers, film, and sheet materials often made via co-extrusion technology^{15,29}.

Polymer blends can be divided into two major classes based on their thermodynamic phase behavior. Miscible blends are homogeneous to the polymer segmental level and a major factor is the energetics of segmental interaction. Very early in polymer science, it was concluded that miscibility among polymer-polymer pairs was a rare exception³⁰. However, research over the last decade has proven this rule to be somewhat overstated^{13,14}. It is generally agreed that the thermodynamic basis for miscibility in polymer blends is an exothermic heat of mixing¹⁴⁻¹⁷ since entropic contributions are so small in such systems. A major thrust of research for more than a decade has been to discover new miscible polymer blends and to understand, in terms of component molecular

structure, the origin of their energetic interactions so that phase behavior in technologically important multicomponent polymer systems may be better controlled or predicted. Very significant advances have been made in this area. Immiscible blends, on the other hand, have phase domains that consist, in the limiting case, of the corresponding pure components. Major variables affecting properties in these cases are the phase morphology and the degree of adhesion between phases. For polymer-polymer composites the phase morphology is predetermined by the process of fabrication (e.g., parallel layers); however, adhesion between these phases is also a critical factor for successful performance. Very often the adhesion at the polymer-polymer interface is poor; and as a result, blends and composites formed from immiscible polymeric components have inferior macroscopic properties owing to the weakness at this interface. This fact limits the use of such multiphase polymer systems.

The following section outlines some of the incentives for polymer blending and gives examples of the types of problems that can be solved by this route. In every case, the property relationships for blends depend critically on control of phase structure. Therefore, subsequent sections will deal with some of the important scientific issues in this area. The first of these is the selection or design of components when a homogeneous or miscible mixture is needed. The second involves phase separated systems where improved interfacial adhesion and morphological control are required, i.e., the concept of "compatibilization." Copolymerization into random, block, or graft structures is shown to be a powerful way of dealing with these problems.

REASONS FOR BLENDING

Polymer blending may be viewed as a problem solving technique and, in most cases, the reasons for selecting this approach fall into two categories: property combinations and cost dilution. Most products succeed because of a beneficial combination or balance of properties rather than because of any single characteristic. In addition, a material must have a favorable benefit to cost relation in order to be selected over other materials for a particular application.

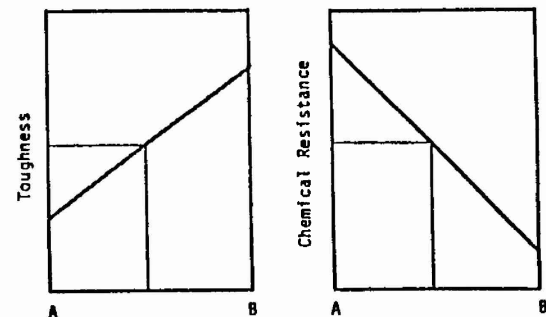


Fig. 1. Illustration of obtaining beneficial property combinations by blending.

The idea of property combinations is best illustrated by an example. Consider an application that requires a material with specified levels of chemical resistance and of toughness. A plastic bumper for automobiles is a typical example. The successful bumper material must be tough enough to survive low speed impacts and must not fail when contacted by gasoline or oil. Polymer A may have more than adequate chemical resistance but insufficient toughness while polymer B is more than tough enough but is lacking in chemical resistance. If blends of A and B exhibit more or less additive values of these two characteristics as illustrated in Figure 1, then certain combinations of these materials may meet both requirements simultaneously whereas neither one alone can. Recently, commercial products of this type have been developed where A is a crystalline, aromatic polyester (e.g., PET or PBT) and B is bisphenol-A polycarbonate²⁸. In other cases, one might seek a favorable balance of processability, flame retardance, stiffness, thermal resistance, barrier properties, etc.

A particular polymer may have a key deficiency that precludes expansion of its application into new areas. By blending this polymer with another that has superior performance in its area of deficiency, one can sometimes broaden its versatility and, thus, its market potential. Table 1 lists a number of polymers that have been the object of intense blend development and some of the characteristics where improvement is sought.

Table 1. Some Frequently Blended Polymers

Polymer	Improvement Sought
PS	toughness (HIPS)
PVC	toughness raise or lower T_g
PPO	processing toughness chemical resistance lower cost
PC	chemical resistance toughness in thick parts
PBT & PET	toughness
ABS	upgrade to engineering thermoplastic level (eg, raise HDT, toughness, chemical resistance)
Nylon	Toughness(dry)

In general, there is a nearly direct relationship between performance and cost among available materials, i.e., high performance materials cost more. This is true because low performance materials that are expensive to produce do not survive. Because of this, some higher performance materials are not able to compete for lower performance markets since there are less expensive materials that will function adequately. Therefore, the producer of a high performance material might seek to broaden market potential through the concept of cost dilution. This is illustrated in Figure 2 where low cost, low performance polymer A and higher cost, higher performance polymer B are blended. If performance is again more or less additive as shown on the left, then a series of lower performance materials may result that can compete with other materials because of the cost dilution factor. Two commercial examples are used to illustrate this principle. The first involves poly(phenylene oxide) as B and polystyrene as

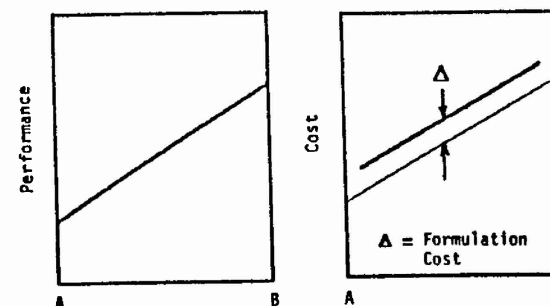


Fig. 2. Concept of cost dilution

A. These two amorphous polymers are miscible and their blends have a single glass transition temperature that progressively increases from that of polystyrene (100°C) up to that of poly(phenylene oxide) (~220°). Thus, blending can give the exact degree of heat resistance, within these limits, required by the application without having to pay for more than is needed. In a similar way, the cost of polycarbonates can be reduced by blending with ABS plastics to gain materials with useful performance/cost ratios. In both of these examples, some other issues are also involved. The processing characteristics of the higher performance poly(phenylene oxide) and polycarbonate are improved by the addition of polystyrene and ABS, respectively.

There is an important caveat, however, about the cost of blends. Their price cannot be the simple tie line connecting those for A and B (see right side of Figure 2) since there is a formulation cost, Δ , that may include extra processing steps, special additives, and a return on the research investment.

Based on the above, blending looks like a simple business where new products can be designed to specification using a computer data base filled with the properties and costs of available materials. However, the property relationships used for illustration purposes in Figures 1 and 2 are rarely so simple. Quite often, arbitrarily chosen components will, in fact, yield blends whose key properties are much worse than additive. That is, the

blend components are incompatible. One must select or design components for blending rather carefully to get the desired result. A key issue is the phase behavior or structure of the blend which is governed by how the components "interact" with each other as illustrated in the following sections. Most successful blends including the examples mentioned above are more than simple mixtures casually put together in an extruder. They are the result of sophisticated materials science that may require specially designed components, modifiers and processing protocols.

MISCIBLE BLENDS

When two polymers, A and B, form a homogeneous mixture, many properties of the blend are additive as implied in the discussions of the previous section^{13,14}. The problem is that most randomly selected polymer pairs are not thermodynamically miscible; hence, homogeneous mixtures are not obtained. The reasons for this are well-known^{13,14}. A necessary thermodynamic condition for miscibility is that the free energy of mixing must be negative and

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (1)$$

sufficient conditions include satisfying additional stability requirements¹³. When A and B have high molecular weights, the favorable entropy term is very small, if not entirely negligible, while the heat of mixing is generally positive and dominates equation 1. The latter term is often expressed in the following van Laar form where the ϕ_i are volume fractions of the components and

$$\Delta H_{\text{mix}} = B \phi_A \phi_B \quad (2)$$

B is the interaction energy density which may also be written in terms of the "chi" notation of the Flory-Huggins theory for polymer mixtures³¹⁻³³.

The usual immiscibility of polymeric components can be circumvented if their segments interact in such a way that the heat of mixing is exothermic or B is negative rather than the usual positive value. Negative B values exist when some appropriate

specific interaction occurs between the segments of the two polymers, and numerous examples of miscible blends based on this principle have been identified over the past decade.²⁸ More recently³¹⁻³³, it has been shown that intramolecular repulsion between monomer units in random copolymers can be an additional driving force causing them to form miscible blends with other polymers. This notion can be very useful for designing polymeric components for formation of miscible blends and, thus, to achieve multicomponent polymer systems with additive properties.

A simple mean field, binary interaction model³¹⁻³³ for copolymer blends gives the following expression for B (equation 2)

$$B = B_{13} \phi'_1 + B_{23} \phi'_2 - B_{12} \phi'_1 \phi'_2 \quad (3)$$

for mixing of a copolymer of monomers 1 and 2 with homopolymer composed of monomer 3. Here, the ϕ'_i indicate the copolymer composition and the B_{ij} characterize the interactions between monomers i and j in the polymers regardless of their bonding to other units. Even though all binary homopolymer pairs may be immiscible, i.e., all $B_{ij} > 0$, certain copolymer compositions may lead to miscible blends ($B < 0$) provided the repulsive B_{12} term in equation 3 is strong enough relative to the other contributions. However, if all of the binary interactions are purely dispersive such that the B_{ij} may be calculated from solubility parameter theory³¹, exothermic mixing cannot result as demonstrated in Figure 3. The example calculation shows that it is possible by copolymerization to match solubility parameters and have B approach zero for a certain composition. This combined with small departures from solubility parameter theory, or weak nondispersive interactions, can evidently lead to regions of compositions where $B < 0$ and, thus, windows of miscibility as seen in many homopolymer-copolymer systems.³¹⁻³³ An interesting example³⁴ is styrene/acrylonitrile copolymers containing from 10 to 30% by weight of AN which are miscible with poly(methyl methacrylate), PMMA.

Random copolymerization can be employed in another useful way to control the phase behavior of blends. Many miscible blends exhibit reversible phase separation on heating, i.e., lower critical solution temperature or LCST behavior. In some cases, the

phase boundary is below the temperature region necessary for melt processing and on cooling a phase separated mixture persists owing to the slow rate at which homogeneity can be achieved. A good example of this is polycarbonate - PMMA blends³⁵. As seen in Figure 4, appropriately prepared blends of these polymers have a single, additive glass transition temperature (left), but the mixture phase separates at temperatures below that needed for melt

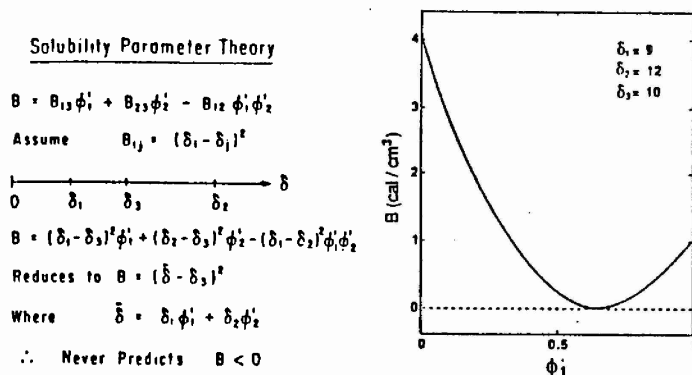


Fig. 3. Calculation of interaction parameters for blends of a homopolymer with a copolymer using solubility parameter theory.

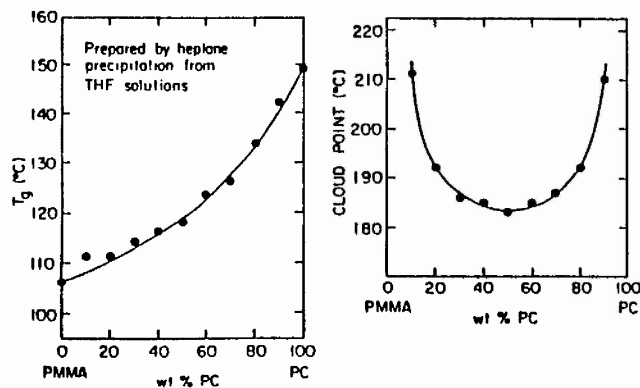


Fig. 4. Phase behavior of blends of poly(methyl methacrylate) and polycarbonate.

processing. Clearly, a method for raising this cloud point curve is needed which amounts to making B in equation 2 more negative. Addition of a comonomer to one of the components has been shown to be a viable approach³⁶⁻³⁹ and may, in principle, function by increasing interchain attraction or by increasing intrachain repulsion or both. Some examples are shown below. More complete details for each case are given elsewhere.³⁶⁻³⁹

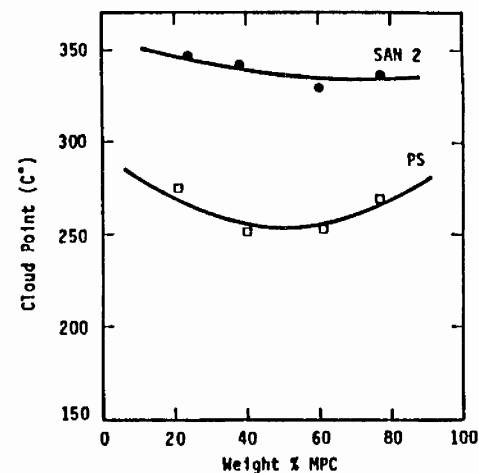


Fig. 5 Cloud point curves for blends of styrenic polymers with tetramethyl bisphenol-A polycarbonate.

Tetramethyl bisphenol-A polycarbonate, MPC, forms miscible blends³⁶ with polystyrene, PS, that phase separate on heating at the temperature shown in Figure 5. By incorporating only 2% by weight of AN into the styrenic raises this boundary by about 80°C. Higher amounts of AN raise this curve to above the decomposition temperature; however, at 13% or more AN the SAN copolymers are not miscible with MPC. Polystyrene forms miscible blends with poly(vinyl methyl ether), PVME, that phase separate at quite low temperatures. Copolymerization of very small amounts of acrylic acid with styrene dramatically elevates the phase separation

temperature³⁸ as seen in Table 2; although, beyond a certain amount of acrylic acid these copolymers are not miscible with PVME. Similar but less dramatic results were obtained using acrylonitrile³⁸, maleic anhydride³⁸, or methyl methacrylate⁴⁰ as the comonomer. Returning to the PC-PMMA system, Figure 6 shows that copolymerizing small amounts of styrene into the acrylic similarly elevates the phase boundary for this system. Equation 3 proves useful for understanding these effects and gives a basis for designing polymers for controlled miscibility.

IMMISCIBLE BLENDS

Blends of immiscible polymers have complex property-composition relationships that are rarely additive. Most properties are dramatically influenced by the spatial arrangement of the phases in the final blend. The morphology is strongly affected by processing history and can change undesirably during fabrication steps since it is a dynamic structure. Properties like stiffness, heat distortion temperature, or barrier behavior are dominated by the component forming the continuous phase and show a sigmoidal shape versus composition owing to phase inversion. Failure properties and toughness are often much less than additive and may be inferior to those of either pure component. This feature severely limits the utility of many potentially valuable blend systems.

The poor mechanical behavior of phase separated blends is usually the consequence of inadequate adhesion between the phases that does not allow efficient transfer of stress across this interface. Poor adhesion results from the lack of affinity between

Table 2. Blends of PVME with Styrene/Acrylic Acid Copolymers

Weight % Acrylic Acid	Miscible with PVME?	LCST
0	Yes	~110°C
1	Yes	Above chemical decomposition temperature
3	Yes	Above chemical decomposition temperature
8	No	..

the two polymers that are responsible for their immiscibility. It is clear that the mechanical properties would be more nearly additive if this interfacial zone were strengthened. One way to do this, shown schematically in Figure 7, is to add interfacially active block or graft copolymer "compatibilizers" to the immiscible mixture.¹⁰ In its simplest form, the compatibilizer has block or graft segments which are chemically identical to those in the respective phases, although non-identical segments which are

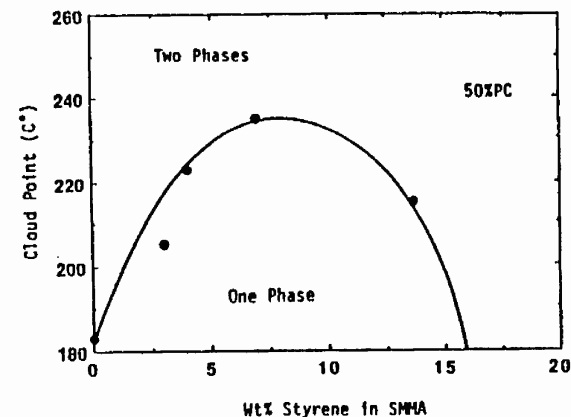


Fig. 6. Effect of styrene comonomer content on temperature of phase separation of polycarbonate blends with methyl methacrylate/styrene copolymers.

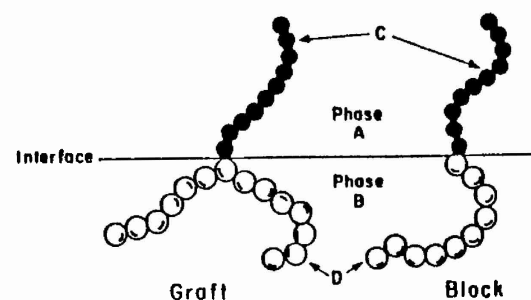


Fig. 7. Compatibilization of immiscible blends with block or graft copolymers at the interface.

Interfacial Block/Graft Reaction Schemes

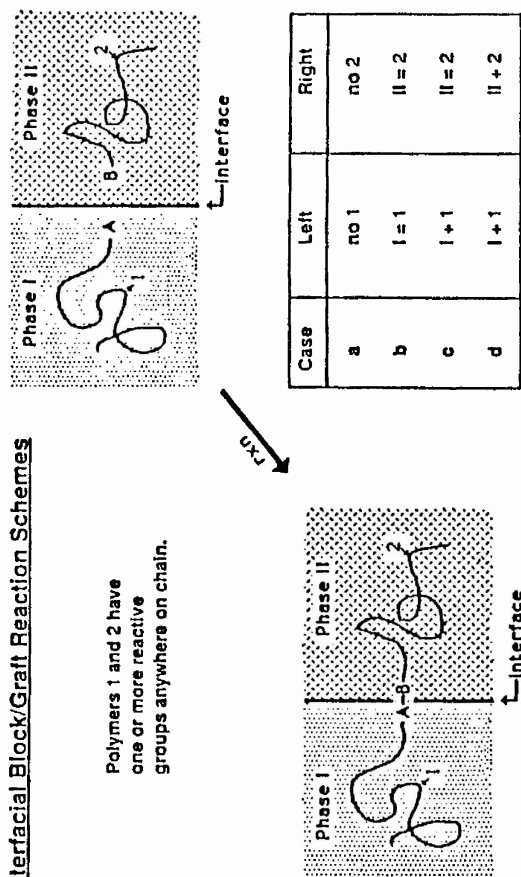


Fig. 8. Compatibilization by reactive processing.

miscible or partially miscible in the respective phases should work equally well to improve interfacial adhesion and blend properties, permit a finer dispersion during mixing, and provide a measure of stability against gross segregation.⁴¹⁻⁵⁵ Some of the most definitive work in this area is that by Teyssie and co-workers⁴³⁻⁴⁹ who have carefully explored compatibilization of immiscible blends containing polyethylene and polystyrene by various hydrogenated butadiene-styrene diblock copolymers. They conclude, based on a combination of microscopy and assessment of mechanical property improvement, that as little as 0.5-2 weight percent addition of diblock is sufficient to achieve a macroscopically homogeneous and stable phase dispersion, that most of the copolymer is at the interface as suggested in Figure 7, that diblock copolymers with blocks of similar size are the most efficient interfacial agents and their activity is effective in a very large range of block copolymer and homopolymer molecular weights for melt blended products, and that diblocks are often more efficient interfacial agents than triblock copolymers and grafts. However, this approach is severely limited by the availability of techniques for preforming appropriate block or graft copolymers. An attractive and generally more useful approach appears to be the formation of such interfacially active species at the interface itself during processing by chemical reactions of functionalized polymer components which are precisely tailored and added in the amount needed. This approach has been described in some recent publications⁵⁶⁻⁵⁸ and is a part of the rapidly growing field known as "reactive processing."

The idea of in situ formation of block or graft copolymer at the polymer-polymer interface is shown schematically in Figure 8. Phase I and Phase II represent the two immiscible polymers, and the diagram shows a small region from a blend or composite that includes a section of interface; Phase I contains polymer chains of type 1 having one or more functional groups (A) anywhere on the chain while Phase II contains polymer chains of type 2 having one or more different functional groups (B). A and B are chosen so that they will readily react with each other to form a block or graft copolymer as shown. Note that this drawing shows only one functional group per chain which is located at the chain end; however, the concept is not limited to this ideal case. The functionalized polymers 1 and 2 must form homogeneous mixtures (i.e.,

miscible) with Phases I and II, respectively. The nature of the interfacial zone may have a significant influence on the ease with which the interfacial reaction can occur. In the limit of a very sharp interface, the A and B groups can approach each other only in very restricted ways (see Figure 9) since they will not be able to penetrate the opposite phase and the probability of reaction will be limited correspondingly. In the more typical case, the interface will be somewhat diffuse, and in this zone, segments from the two phases will intermix creating greater opportunities for A and B groups to approach each other (as shown schematically on the right in Figure 9) and subsequently to react.

These approaches to compatibilizing immiscible blends allow the development of unique products not limited by the immiscibility of the components⁵⁹ and offer the opportunity for many exciting "new" materials.

SUMMARY

In principle, polymer blending is an attractive physical alternative to new molecules for developing new products. However, to practice this approach successfully requires careful control of phase structure since this affects the properties that can be achieved. Through appropriate copolymerization methodology one can manipulate miscibility, phase morphology, and interfacial adhesion to achieve highly engineered blend materials having properties that are additive combinations of the components. In some

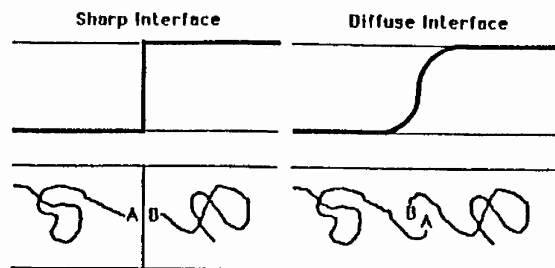


Fig. 9. Reaction configuration at sharp and diffuse interfaces.

cases, individual properties can be better than those for either component, i.e., synergism can occur.

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